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DEVELOPMENT OF TECHNIQUES FOR PREPARING  
HOMOGENEOUS SINGLE CRYSTALS OF LEAD  
TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

J.F. Miller, et al

Battelle Memorial Institute  
Columbus, Ohio

15 July 1966

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FINAL REPORT

on

DEVELOPMENT OF TECHNIQUES FOR PRE-  
PARING HOMOGENEOUS SINGLE CRYSTALS OF  
LEAD TELLURIDE, LEAD SELENIDE,  
AND LEAD SULFIDE

to

MASSACHUSETTS INSTITUTE  
OF TECHNOLOGY

July 15, 1966

by

J. F. Miller, J. W. Moody, and R. C. Himes

Subcontract No. 212 of Prime  
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July 28, 1966

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Attention Mr. R. S. Clarke  
Distribution Office

Gentlemen:

Enclosed are ten copies of the Final Report on the project, "Development of Techniques for Preparing Homogeneous Single Crystals of Lead Telluride, Lead Selenide, and Lead Sulfide", Subcontract No. 212 of Prime Contract No. AF 19(628)-5167. This report summarizes research done in the period from July 15, 1965, to July 15, 1966.

Copies of the report are being distributed to individuals and organizations on the approved distribution list in accord with the agreement.

Very truly yours,



J. F. Miller  
Associate Chief  
Physical Chemistry Division

JFM:cm  
Enc. (10)

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DEVELOPMENT OF TECHNIQUES FOR PREPARING  
HOMOGENEOUS SINGLE CRYSTALS OF LEAD TELLURIDE,  
LEAD SELENIDE, AND LEAD SULFIDE

by

J. F. Miller, J. W. Moody, and R. C. Himes

INTRODUCTION

This final report summarizes research done from July 15, 1965, to July 15, 1966. Annual summaries of research accomplished on the project also may be found in the Summary Report of July 15, 1963; the Twelfth Quarterly Progress Report, September 9, 1964; and the Sixteenth Quarterly Progress Report, July 15, 1964.

SUMMARY

The results of research in this annual period showed that vacuum sublimation can yield PbTe with high apparent electron mobilities, i.e.,  $R\sigma > 10^6 \text{ cm}^2/\text{v-sec}$ , at liquid-helium temperature. However, examination of the crystals revealed the presence of a second (Pb-rich) phase, and results of electrical-property studies suggest that the high mobilities may be due to the presence of the second phase.

The results of studies of the doping of PbTe with Hg and Pt, although not conclusive with regard to Hg, indicated that Pt is a donor in PbTe that appears to react with intrinsic defects in such a way that free-carrier concentrations and carrier scattering are reduced. High-mobility Pt-doped crystals were prepared with 77 K carrier concentrations as low as  $5 \times 10^{16} \text{ cm}^{-3}$ .

Several techniques, including growth from the melt, vapor growth, solution growth, and heat treatment, were investigated for the preparation of low-carrier-density crystals of PbTe-SnTe alloy. The better crystals, with carrier concentrations in the  $10^{17}$  and  $10^{16} \text{ cm}^{-3}$  ranges were prepared by vapor growth. Although large crystals of PbTe and PbTe-SnTe alloy were grown from solution, further development of the method is required.

Accepted for the Air Force

Franklin C. Hudson

Chief, Lincoln Laboratory Office

EXPERIMENTAL DETAILS AND DISCUSSION

Vacuum Sublimation of PbTe

Investigation conducted on the vacuum sublimation of PbTe was concerned with the effect of multiple sublimations, with heat treatment of crystals of the vacuum-sublimed

PbTe, and with the electrical properties of the crystals at temperatures down to 4.2 K, and with analysis of selected crystals.

Study of the multiple sublimation of n-type PbTe revealed that, whereas crystals having relatively high  $R\sigma$  values (at 77 K) are obtained after one or two sublimations,  $R\sigma$  values are low for crystals grown from material that has been vacuum sublimed three or four times at 700 to 800 C. Heat treatment of these crystals at 822 C under standard conditions developed previously on this project was found to increase 77 K  $R\sigma$  values to a uniformly high level similar to that usually observed for other specimens of pure (but not vacuum-sublimed) PbTe.

Although the electrical properties of vacuum-sublimed PbTe were similar at 77 K to those of normally prepared PbTe, electrical-property determinations down to 4.2 K revealed significant difference.  $R\sigma$  values in excess of  $10^6 \text{ cm}^2/\text{v-sec}$  at 4.2 K and up to  $10^7 \text{ cm}^2/\text{v-sec}$  were observed for crystals of the vacuum-sublimed material, whereas those for crystals of normally prepared PbTe fell generally in the range  $10^4$  to  $10^5 \text{ cm}^2/\text{v-sec}$ .

Comprehensive study was made of PbTe crystals exhibiting the exceptionally high  $R\sigma$  values of  $10^7$  and  $1.8 \times 10^6 \text{ cm}^2/\text{v-sec}$ . No significant deviation of the precision X-ray lattice constant for the material from the accepted value for PbTe was found. However, electrical-property versus temperature measurements that showed an abrupt, order-of-magnitude increase of electrical conductivity with increasing temperature at about 6.1 K for the crystal exhibiting the  $10^7 R\sigma$  value, indicate the possibility of the onset of superconductivity in a Pb-rich phase, since this temperature is near the transition temperature for Pb. Supporting evidence was found in metallographs of the crystal that showed a second, apparently Pb-rich, phase distributed along the 100 crystallographic planes.

No abrupt change in electrical conductivity with temperature was observed for the second crystal ( $R\sigma = 1.8 \times 10^6 \text{ cm}^2/\text{v-sec}$ ). Metallographic examination revealed the presence of a second (Pb-rich) phase, but the concentration was lower than that in above-discussed material, and the precipitated phase was distributed randomly.

The findings of this portion of the investigation suggest that the very high mobilities ( $R\sigma$ ) reported for PbTe are not an intrinsic characteristic of the pure compound.

#### Mercury-Doped PbTe

It was shown by direct analysis that Hg concentrations are highest in the first-to-freeze portion of Bridgman-grown crystals of PbTe. The distribution may not, however, be attributable solely to segregation in the solid-liquid system since the Hg readily can be redistributed through the vapor phase.

Studies were carried out on as-grown and heat-treated Hg-doped PbTe. Properties of the Hg-doped crystals were not found to be significantly different from those of undoped PbTe prepared similarly. The role of Hg as a dopant in PbTe (i. e., donor or acceptor) therefore was not established.

### Platinum-Doped PbTe

It was shown by direct analysis that Pt concentration is lowest in the first-to-freeze portion of a Bridgman-grown crystal, and that Pb concentration increases with progression toward the last-to-freeze end of the crystal - as is normal for an impurity that lowers the melting point of a substance. Studies were made of the electrical properties of as-grown and heat-treated crystals of Pt-doped PbTe. It is indicated that Pt is a donor in PbTe that can be utilized to prepare low-carrier-density, high-electron-mobility crystals. The observed properties apparently result from the interaction of Pt with intrinsic defects. Utilizing Pt as a dopant, crystals with free-carrier concentrations as low as  $4.8 \times 10^{15} \text{ cm}^{-3}$  were prepared, and crystals with  $R\sigma$  values as high as  $38,000 \text{ cm}^2/\text{v-sec}$  at  $77 \text{ K}$  ( $n = 6.5 \times 10^{16}/\text{cm}^3$ ) were prepared.

"Aging" at room temperature was observed for the Pt-doped crystals. Two types of effects were observed: one resulting in an increase in resistivity, and a second resulting in an increase of carrier concentration. Further study is needed to elucidate the aging process(es) in Pt-doped PbTe.

### Preparation of PbTe-SnTe Alloy Crystals

Research was carried out on the preparation of crystals of the PbTe-SnTe alloy. Several approaches to the preparation were investigated: growth by melt techniques, growth from the melt followed by heat treatment, growth from solution, and growth by vapor techniques.

#### Melt Growth

Crystals of SnTe and ingots of PbTe-SnTe alloy were grown from metal-rich melts by the Bridgman method at drop rates from 1.2 to 5.0 cm/hr. The 50-50 and 33-66 mole ratios were selected as initial compositions of the PbTe-SnTe melts since these liquidus compositions correspond to solidus compositions near 90-10 and 77-23 PbTe-SnTe, respectively.

Large crystals, of centimeter dimensions, were grown in the SnTe ingots. Crystals were smaller in the alloy ingots - being of millimeter cross-sectional dimensions.

All of the crystals grown from the melt, both of SnTe and of the PbTe-SnTe alloy, were p-type with low electrical resistivity and Hall coefficient, as expected. These melt-grown crystals were employed in heat-treatment experiments.

#### Heat Treatment

A large number of SnTe and PbTe-SnTe alloy crystals were heat treated in the vapor of metal-rich PbTe-SnTe alloy, Sn, Pb, Zn, or Cd at temperatures in the range, 450 to 800 C for periods of 2 to 10 days. In addition to these high-temperature heat treatments, many of the specimens were then heat treated at 400 and 300 C for 3 to 7 days at each temperature.

All of the SnTe and PbTe-SnTe alloy crystals remained p-type. However, several of the alloy crystals had measurable Hall coefficients following the heat treatment.  $R_O$  values (at 77 K) ranged up to  $600 \text{ cm}^2/\text{v-sec}$ , increasing with decreasing heat-treatment temperature and with maximum values observed for specimens heat treated at 650 C. In a series of heat-treated SnTe crystals, electrical resistivity appeared to increase as heat-treatment temperature was decreased in the range 750 to 550 C.

#### Vapor Growth of PbTe-SnTe Alloy

A number of vapor-growth experiments were conducted utilizing as source materials crushed, metal-rich PbTe-SnTe alloys of the 90-10, 85-15, 80-20, 75-25, and 70-30 (mole-ratio) compositions that had been homogenized in the molten state and quenched. The crystal growth was conducted in sealed, fused-silica ampoules that either were evacuated or contained about 1/3 atm of  $\text{H}_2$  (at 300 K), with source temperatures in the range 660 to 840 C and with temperature gradients of 1 to 100 C/cm. Total temperature differentials ranging from negligible values to about 700 C were employed.

Alloy crystals of millimeter dimensions were successfully grown. The largest crystals were obtained in 750 to 820 C temperature zones with temperature gradients near 10 C/cm and in evacuated ampoules rather than in a partial atmosphere of hydrogen. Both n- and p-type crystals were prepared with 77 K carrier concentrations in the  $10^{16}$  and  $10^{17} \text{ cm}^{-3}$  ranges for crystals of the 85-15 and 80-20 PbTe-SnTe compositions. Electron and hole mobilities at 77 K (i.e.,  $R_O$  values) as high as 33,000 and 43,000, respectively, were observed for alloy crystals of these approximate compositions.

#### Solution Growth of PbTe and PbTe-SnTe Alloy

A portion of the research was directed toward the development of a method for the growth of crystals from solution in the constituent metals at relatively low temperatures. Crystals of PbTe and 80-20 PbTe-SnTe alloy with dimensions up into the 1 to 2 cm and 0.5 to 1 cm ranges, respectively, were grown in solutions of about 10 weight percent Te in the metals by a slow-cool procedure in which temperature was decreased at a uniform rate of 0.4 C per hour from 750 to 400 C.

The solution-grown crystals of both PbTe and the PbTe-SnTe alloy were of cubic habit. The growth generally was hoppered, however, and where the cube faces had filled in, layers of entrapped solvent metal were observed between 100-plane lamellae of the compound crystals. Crystals were also grown at a cooling rate of 0.8 C per hour in an effort to minimize the hoppered habit by increasing the supersaturation of the solution. However, the results were similar to those obtained at the slower growth rates.

The results of electrical-property measurements made on crystals selected to avoid the microscopically visible metal inclusions revealed that carrier concentrations in the solution-grown crystals were high - in the  $10^{18}$  and  $10^{19} \text{ cm}^{-3}$  ranges for PbTe and the alloy, respectively. The PbTe crystals were n-type as expected, but the Hall

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measurements unexpectedly indicated that the 80-20 PbTe-SnTe alloy crystals were p-type.

\* \* \* \* \*

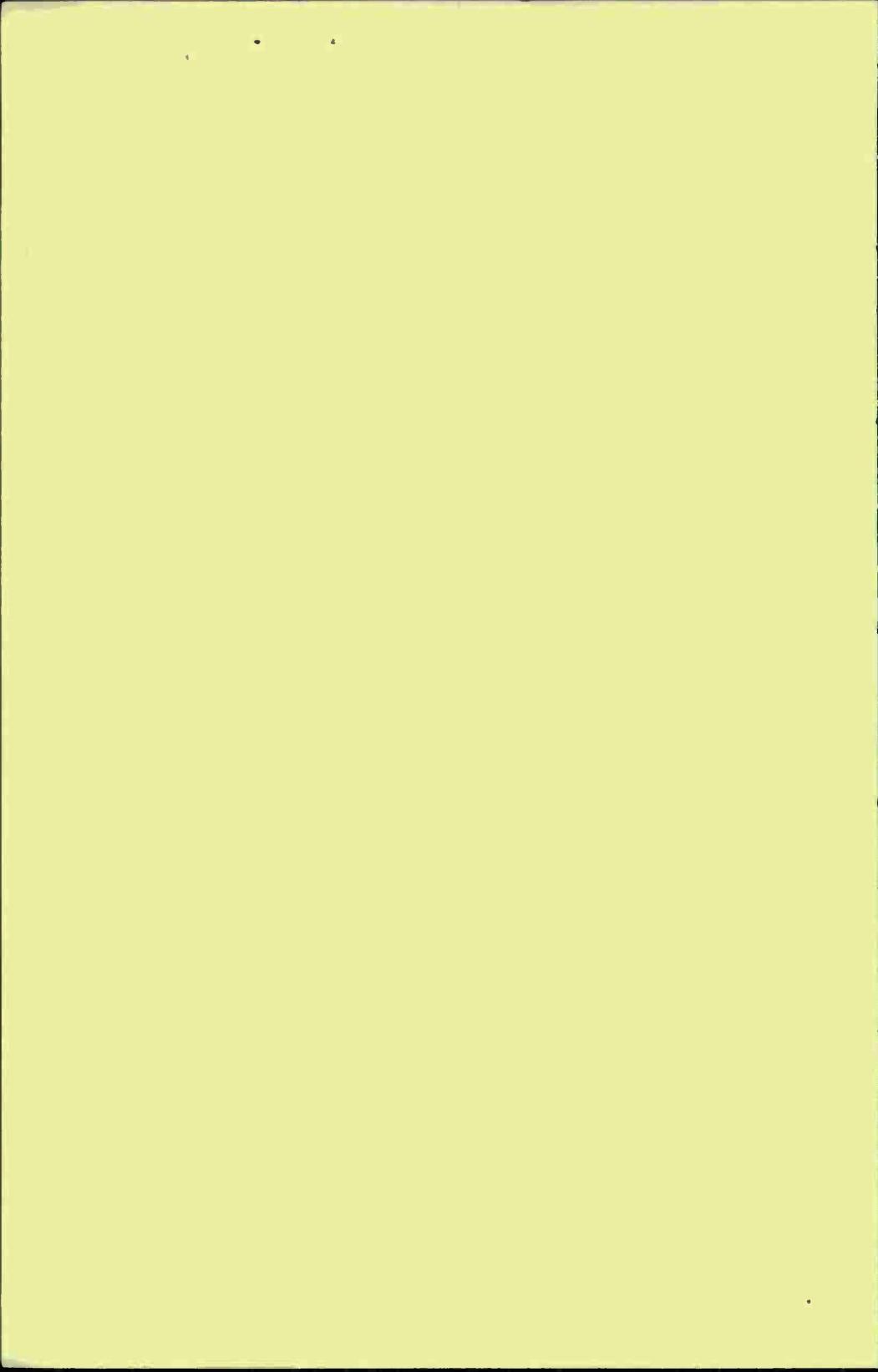
Data upon which this report is based are recorded in Battelle Laboratory Record Books 21321, pp 73-100, and 23046, pp 1-100.

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